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Impact Event at the Permian-Triassic Boundary: Evidence from Extraterrestrial Noble Gases in Fullerenes

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The Permian-Triassic boundary (PTB) event, which occurred about 251.4 million years ago, is marked by the most severe mass extinction in the geologic record. Recent studies of some PTB sites indicate that the extinctions occurred very abruptly, consistent with a catastrophic, possibly extraterrestrial, cause. Fullerenes (C_{60} to C_{200}) from sediments at the PTB contain trapped helium and argon with isotope ratios similar to the planetary component of carbonaceous chondrites. These data imply that an impact event (asteroidal or cometary) accompanied the extinction, as was the case for the Cretaceous-Tertiary extinction event about 65 million years ago.

The extinction event that marks the Permian-Triassic boundary (PTB) [251.4 ± 0.3 million years ago (Ma)] was the most severe in the past 540 million years (*1*), killing off over 90% of all marine species, ~70% of terrestrial vertebrate genera, and most land plants (*2–5*). Several new studies have shown that these extinctions were much more abrupt than previously thought (*6–8*), with estimates of the extinction interval ranging from <500,000 years (*6*) to ~8000 years (*8*). Proposed catastrophic hypotheses for the PTB extinction event include bolide impact (asteroidal or cometary) (*9*) and/or massive flood basalt volcanism (*10*). The radiometric ages of the Siberian Flood Basalt volcanism (251.2 ± 0.3 Ma) (*6*, *10*) suggest that the volcanism was coincident with the time of the PTB extinction event. Other extinction mechanisms involving ocean anoxia as well as changes in sea level and climate have also been proposed (*1*, *11*, *12*).

The suggestion by Alvarez *et al.* (*13*, *14*) that bolide impact was the ultimate reason for the mass extinction observed at the 65–million year Cretaceous-Tertiary boundary (KTB) led to the assumption that all such events were associated with an extraterrestrial (ET) cause. Despite a compelling ET scenario developed for the KTB (supported by the presence of iridium, shocked quartz, and microspherules), the cause of the PTB mass extinction remains unresolved. One of

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the problems with an ET trigger for the PTB event is that there is no significant iridium anomaly at the PTB (*15*, *16*) that is comparable to the KTB iridium enrichments of 10 to 100 times above background levels (*13*, *14*). Quartz grains showing deformation features have been reported at two PTB boundary sections (*16*), but the evidence for shock metamorphism is still considered equivocal. Here we report that some PTB sediments contain fullerenes with trapped noble gases that are indicative of an ET source.

Fullerenes have been previously associated with two separate events involving the impact of a large bolide with Earth: (i) in the 1.85-billion-year-old carbon-rich breccias (Onaping formation) at the Sudbury crater (*17*, *18*) and (ii) in clay sediments from the 65-million-year-old KTB layer (*19*, *20*). The fullerenes in both deposits contain noble gases encapsulated within the "cages" of the fullerene molecules (*20*). The isotopic compositions of the gases are similar to those found in meteorites and some interplanetary dust particles (IDPs) (*17*, *20*) but are unlike that of Earth's atmosphere. Fullerenes (C_{60} to C_{400}) have now been isolated from the Murchison and Allende carbonaceous chondrites that have He and Ar isotopic ratios that can only be explained as ET in origin (*20*). Based on these findings, it appears that fullerenes form in an ET environment, are exogenously delivered to Earth in some meteorites or comets, and are preserved in impact deposits associated with a major extinction event.

Fullerene (C_{60} and C_{70}) has been reported in PTB sediments from Inuyama, Central Japan (*22*), and is linked to extensive wildfires (*19*) on the supercontinent Pangea and subsequent deposition on an anoxic deep-sea floor of the superocean Panthalassa. However, unlike the KTB, the PTB has no corresponding soot material within the boundary layer, a diagnostic indicator of biomass burning triggered by the impact event (*23*, *24*). In this study, we measured the isotopic compositions of the encapsulated noble gases to determine the environment of fullerene formation (*17*, *20*, *25*).

The fullerene spectrum and encapsulated noble gases were examined in sediments from three PTB locations: the classic PTB section at Meishan, South China; the Sasayama section, in southwest Japan; and the Bálvány section, in the Bükk mountains in Northern Hungary (*26*–*31*). The Meishan PTB sediment corresponds to boundary layer bed 25: a white clay layer, described in (*6*, *7*). Most of the shallow-water marine species disappeared within this short interval and near the base of bed 25, where the extinction rate reaches 94%. Estimated accumulation rates for the transitional beds (beds 24 through 27), based on radiometrically dated ash layers, are unusually low (~0.03 cm per 1000 years), suggesting hiatuses (*7*). Samples were collected at the base of bed 25 and from bed 33 (~225 cm above the Meishan PTB) and bed 17 (~2 m below the Meishan PTB).

The Sasayama PTB is a deep-water facies composed of bedded cherts and shale (red to gray) overlain by a 0.8-m-thick siliceous shale. Directly above the siliceous shale is a 1-m-thick sheared black shale that is capped by a 1.2-m interval of thinly interbedded green-grey siliceous shale and chert. The boundary layer is identified by studies of radiolarians within the bedded cherts and the siliceous shales. Sedimentation rates for the siliceous shale and black shale are low and are estimated at ~0.7 cm per 1000 years (*28*). We examined samples at intervals of 3 to 5 cm as well as 30 cm above and 85 cm below the Sasayama PTB.

The Bálvány, Hungary, boundary clay is a shallow-water facies embedded in limestones with black fauna-rich fossil layers (Upper Permian, ~2 m thick) below and the Lower Triassic Gerennavár limestone (~6 m thick) above, and is identified as a reddish-colored clay layer ~1 cm thick. The boundary layer is further characterized by a rapidly diminishing occurrence (about a few centimeters) of Permian fossils that disappear in the early Triassic (*26, 27*). The Hungary section is similar in lithology to sections in the Italian and Austrian Alps (*31*), where sedimentation across the boundary has been estimated at rates as high as ~6 to 10 cm per 1000 years (*8*). Samples were examined at intervals of 3 to 5 cm and at 85 cm above and below the boundary.

The sediment samples were demineralized and extracted with organic solvents, such as toluene (*17*, *20*, *32*–*34*). Laser desorption mass spectrometry (LDMS) analysis of the toluene (*35*) extract for the Meishan, China, sediment showed a peak at a mass-to-charge ratio (m/z) of 720 atomic mass units (amu), which corresponds to C_{60}^+, and a peak at 840 amu, which corresponds to C_{70}^+ (~5 μg). Similar results were obtained for the Sasayama sample; however, no mass peaks corresponding to C_{60}^+ and C_{70}^+ were detected in the Bálvány, Hungary, toluene extract [amounts of C_{60}^+ and C_{70}^+ were <50 ng or 1 part per billion (ppb)]. We extracted the sediment samples a second time with 1,2,3,5-tetramethylbenzene (TMB), a solvent with a high boiling point, to isolate the larger fullerene cages (*20*, *32*–*34*). LDMS analyses of the TMB fullerene extract residue (~14 μg) revealed a small mass peak for C_{60}^+ and a much more prominent high-mass envelope that dominated the spectrum between C_{70}^+ and C_{200}^+ (Fig. 1B). These higher fullerene-related carbon clusters were separated by 24 amu or by a C_2^+, which is a diagnostic indicator that the high-mass envelope detected in the TMB residue was composed of pure carbon clusters rather than some other molecule or compound (*20*, *34*). Moreover, no fullerenes (amounts were <50 ng or 1 ppb) were detected in beds 33 and 17 above and below the Meishan PTB.

The TMB extract for Sasayama (~10 μg) displayed much more prominent mass peaks for C_{60}^+ and C_{70}^+ and a limited series of higher fullerenes (Fig. 1C) between C_{70}^+ and C_{140}^+. We attribute the lower abundance of higher fullerenes to degradation in the Sasayama PTB sediments, possibly as a result of later tectonism (*28*, *36*). Sediment residues from the cherts above and below the PTB layer have fullerenes at or below the blank level (50 ng or 1 ppb), which suggests that the fullerene signal is recording a short-term event rather than the continuous deposition of IDPs to the sediments (*37*). The TMB extract from the Bálvány, Hungary, PTB indicated a weak signal for C_{60}^+ and C_{70}^+ and some higher fullerenes; however, the yield of fullerene was extremely low (<1 μg). Samples of limestones above and below this layer were also devoid of fullerene (<50 ng or 1 ppb). Either the environment of deposition and/or subsequent geologic processing over some 250 million years was not conducive to fullerene preservation at Bálvány, or the sediment layer examined in this study is not at the PTB.

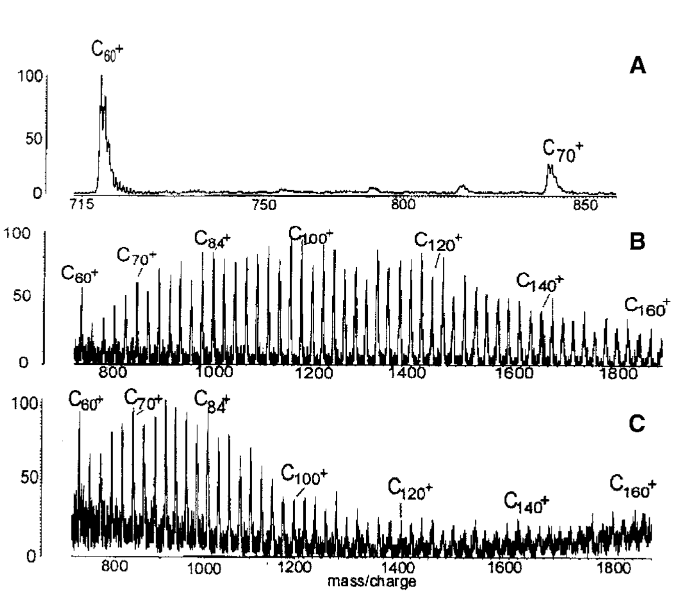


Fig. 1. LDMS of the Meishan, China, and Sasayama, Japan, boundary sediments. (**A**) LDMS spectrum of Meishan (toluene) extract, showing peaks at m/z of 720 and 840 amu (C_{60}^+ and C_{70}^+). (**B**) LDMS spectrum of Meishan (TMB) extract, showing a small mass peak for C_{60}^+ and a range of larger carbon clusters between C_{70}^+ and C_{160}^+. (**C**) The higher fullerenes in the Sasayama (TMB) extract.

The helium isotopic compositions of fullerenes from both the Meishan and Sasayama PTB boundary sites are within the range reported for the "planetary" component in meteorites (1.6 to 1.9 × 10^{-4}) (38). For comparison, a new high-quality noble gas analysis of the fullerene component in the Murchison carbonaceous chondrite was also evaluated. The total helium concentrations in the two PTB boundary samples were also similar (0.1 to 0.2 μcc of ^{3}He/g) and were equivalent to those in the Sudbury fullerenes (17). The ET signature of the helium provides strong evidence that the PTB fullerenes were delivered intact to Earth in a bolide (asteroidal or cometary) at the PTB. To confirm that the increase in the fullerene component at the PTB results from an impact and not from a change in the sedimentation rate at the boundary, we examined the ^{3}He concentration in the bulk Sasayama sediments at several intervals (Fig. 2). At Sasayama, the bulk ^{3}He actually decreases at the boundary, whereas the concentrations of fullerene and fullerene-encapsulated ^{3}He increase more than 50-fold. The fullerene-encapsulated ^{3}He represents almost 50% of the total ^{3}He in the bulk sediments, as opposed to <1% above and below the boundary. The magnitude of this unique ^{3}He signal at the boundary points to a discrete event, in contrast to the signal that would have been produced by deposition to the deep-sea sediments from a continuous IDP source (39–41).

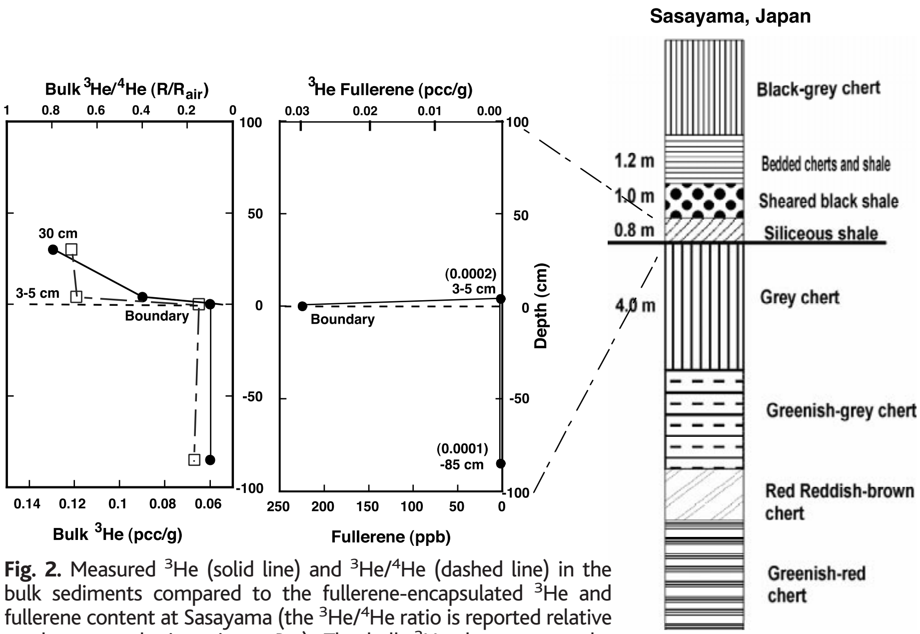
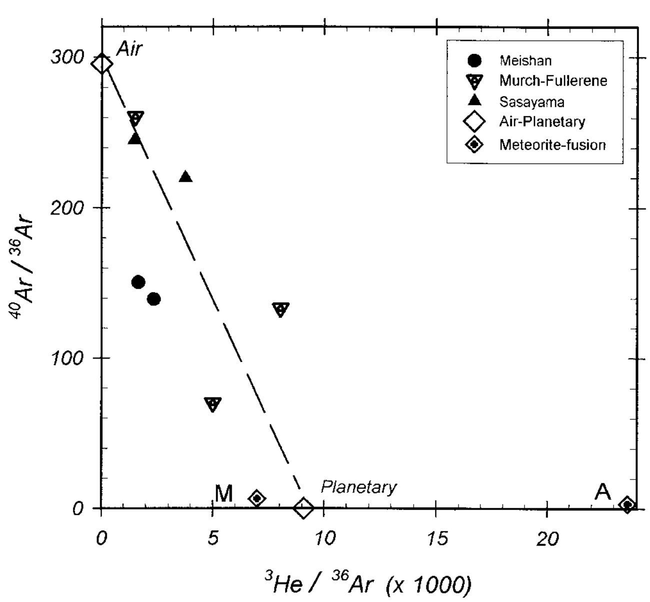


Fig. 2. Measured ^{3}He (solid line) and ^{3}He/^{4}He (dashed line) in the bulk sediments compared to the fullerene-encapsulated ^{3}He and fullerene content at Sasayama (the ^{3}He/^{4}He ratio is reported relative to the atmospheric ratio or R_{air}). The bulk ^{3}He decreases at the boundary in comparison to samples above and below, whereas the fullerene and fullerene-encapsulated ^{3}He concentrations increase by 50-fold. The fullerene-encapsulated ^{3}He represents roughly half of the total ^{3}He in the bulk sediments as opposed to <1% above and below the boundary. Variations in the ^{3}He concentration for the bulk sediments may be attributed to fluctuating sedimentation rates, sediment focusing (41), or variability in the flux of IDPs to Earth over geologic time (40). Similar results were obtained for the fullerene-encapsulated ^{3}He above and below the boundary at Meishan (see Web table 1, available on *Science* Online at www.sciencemag.org/cgi/content/full/291/5508/1530/DC1).

Fig. 3. A plot of the measured ^{40}Ar/^{36}Ar ratios versus the ^{3}He/^{36}Ar ratios in PTB deposits and Murchison indicates a mixing trend between atmospheric (295.5, <0.001) and planetary (<1, 0.01) components. These symbols denote measurements made for both PTB samples and the Murchison meteorite fullerene-encapsulated ^{3}He component. Also plotted are the bulk acid residues for the Murchison (M) and Allende (A) carbonaceous chondrites after extraction of the fullerene component (28).



Measured ^{40}Ar/^{36}Ar ratios of 70 to 220 in the boundary sediments also demonstrate an ET origin for the fullerenes. The fraction of meteoritic ^{36}Ar varies between 25 and 75% with an atmospheric ^{38}Ar/^{36}Ar ratio, consistent with a planetary component (38, 42). In support of the hypothesis that a planetary gas reservoir existed at the time of fullerene formation (as opposed to a solar gas reservoir), the ratio of ^{3}He/^{36}Ar resembles most closely the planetary ratio (Fig. 3) present in carbonaceous chondrites (38, 42). The data fall off the "perfect" air-planetary gas mixing line because of the preferential release of He relative to Ar during extraction. Mixing with a solar gas component (^{3}He/^{36}Ar = ~1) clearly does not fit the measured He-Ar isotopic systematics. The neon isotopic ratios also support a planetary gas reservoir, although the evidence is not as strong (43, 44).

Because of the known property of fullerenes of incorporating noble gases as a direct function of the partial pressure of the gas [according to the rigid sphere model (25)], the data suggest a partial pressure in the environment of formation equivalent to ~2 to 4 atmospheres of He. Only stars or collapsing gas clouds (17) have significant helium pressures and provide an environment of formation conducive to fullerene synthesis (that is, with low H/C ratios). Overall, the light noble gas data for two PTB deposits and the Murchison carbonaceous chondrite show consistent results that point to a planetary gas reservoir at the time of fullerene formation (38, 45). Synthesis of fullerenes during impacts on Earth or in space would not lead to high noble gas concentrations with this distinctively planetary chemical and isotopic signature. This planetary signature dominates the noble gas isotopic composition of the PTB sediments and the carbonaceous acid residue for Allende and Murchison, although the yields of the fullerene carrier phase are much lower (46, 47).

Thus, it would appear that ET fullerenes were delivered to Earth at the PTB, possibly related to a cometary or asteroidal impact event. Based on the measured ^{3}He content for the PTB and Murchison fullerenes, the estimated size of the bolide is 9 ± 3 kilometers or comparable to the KT Chicxulub impactor (48). Such an event could have caused the severe end-Permian mass extinction. Our results are consistent with recent paleontological studies that now point to a very rapid extinction event. The unique planetary signature measured in fullerenes isolated from the Murchison carbonaceous chondrite and from the PTB sediments demonstrates that this distinctive noble gas carrier can survive major impact events and contribute to the unique gas signature of the terrestrial planetary atmospheres.

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26. The Meishan clay layer, the best studied and most complete PTB section, was collected by Sam Bowring (*6*). The Sasayama PTB bedded cherts (collected by Michael Rampino) are identified by radiolarians of *Pseudoalbaillella longtanensis, P. globosa, Follicucullus monacanthus, F. japonicus, F. c. harveti*, and *Neoalbaillella ornithformis* zones in descending order, indicating a mid- to late Permian age. The lower siliceous shale revealed no age-diagnostic fossils. The interbedded siliceous shale and chert revealed *Neospathodus waagen* and *Ns. Dieneri,* indicative of a Smithian age (late Early Triassic). The Bálvány PTB sediments (collected by Michael Rampino) are identified by the disappearance of rich late Permian shelf fauna (*30*) and the appearance of disaster fauna and flora composed largely of foraminifera Earlandia and Gymnocodium alga. The Triassic section contains rare Conodonta and Foraminifera faunas. Microspherules have been reported in the boundary sediments from Meishan (*7*), Sasayama, and Bálvány (*28–30*). In addition, there are reports of iridium enrichments of 10 times background levels at some PTB locations (*15*, *23*).
27. The Sasayama Permian-Triassic section (35°4′N, 135°13′W) is exposed in a cut along a logging road in the city of Sasayama, Fujioka-Oku district in Hyogo Prefecture, southwestern Honshu. The Bálvány, Hungary, PTB (48°6′N, 20°28′E) in the Bükk mountains is exposed in a road cut in a forest on the northern side of the Bálvány mountain, ~100 m from the motorway between Garadna Valley and Bánkùt.
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32. The PTB sediments were first demineralized with hydrofluoric acid and boric acid (BO_3) to concentrate the carbonaceous fraction (*33*). These residues were refluxed with an organic solvent (toluene) in a Soxhlet extraction vessel to extract C_{60} and C_{70} (*20*). The same carbonaceous residues were refluxed a second time with TMB, a solvent used to isolate the higher fullerenes [C_{100} to C_{400} (*20*)]. LDMS (*17*, *20*) identified the diagnostic mass spectrum of the fullerene component. The remaining TMB and toluene extracts were evaporated to dryness in preparation for noble gas analyses.
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35. The toluene extract generated only a small percentage of the total fullerene component, because most of the extracted fullerenes dissolved in the solvents with higher boiling points [TMB and TCB (1,2,4-trichlorobenzene) (*20*)].
36. The fullerenes in the Sasayama cherts are clearly less well preserved than those in the Meishan clay (Fig. 1, A and B). This is also evident when comparing these results to the KTB clays examined in (*20*). The stability of the fullerene cage favors C_{60}^{+} and the lower fullerenes (C_{70}^{+} to C_{100}^{+}), as observed in the Sasayama spectrum (Fig. 1C). The lithology of clay versus chert, which is indicative of the environment of deposition, also appears to be important to fullerene preservation (Fig. 1, B and C). This is in contrast to the large fullerene clusters observed in both the Murchison and Allende carbonaceous chondrites (up to C_{400}^{+}), which are protected from degradation within the meteorite rock matrix (*20*). Fullerene is highly resistant to metamorphism [as in the Sudbury crater samples (350° to 400°C or greenschist facies)], which is why fullerene is such a robust tracer in the geological environment.
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39. Because interplanetary dust is very high in ^{3}He, continuously bombards Earth, and accumulates in sediments, any change (or hiatus) in sedimentation can result in an apparent spike (or drop) in the ^{3}He concentration (measured per gram of sediment). For example, in slowly accumulating oceanic sediments [as in sample GPC-3, a piston core of pelagic clay from the central North Pacific (30°19′N, 157°49.9′W)], the ^{3}He in the bulk sediments varies from 6 to 106 pcc/g (*40*), which is about 20 to more than 200 times greater than the ^{3}He at Sasayama (sedimentation rates are comparable at ~0.03 to 0.1 cm per 1000 years). These variations in ^{3}He concentration are caused by fluctuating sedimentation rates, sediment focusing, and/or variability in the IDP flux to Earth (*40*, *41*). Most of this IDP ^{3}He in the GPC core is produced by high-energy cosmic ray bombardment of silicates, with a maximum of 1% of the ^{3}He occurring in a solvent-extractable fullerene component (L. Becker, R. J. Poreda, unpublished data).
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43. The $^{20}Ne/^{22}Ne$ ratios of 9.5 ± 0.40 suggest mixing between atmospheric and planetary components, with a maximum percent of planetary Ne of only ~ 30%. At these low Ne concentrations for Meishan and Sasayama, the ^{20}Ne and ^{22}Ne signals are affected by interference peaks ($^{40}Ar^{++}$ and CO_2^{++}) and by blank contributions that contribute to the analytical uncertainty. Kr and Xe data, although extremely useful, were not obtained because of the necessity of using liquid nitrogen to minimize the migration of the hydrocarbon breakdown products of the fullerene. The $^{20}Ne/^{22}Ne$ values trend toward Ne-A values (planetary) rather than solar neon values (Ne-B = 13.5). The air component cannot be removed completely, because it most likely resides within the fullerene cage and is released throughout all heating steps rather than existing as an external absorbed component.
44. Noble gas isotope ratios were measured on the VG 5400 noble gas mass spectrometer (*49*). All gases were compared to a calibrated air standard, and the $^{3}He/^{4}He$ ratio is reported relative to the atmospheric ratio R_{air}. The standard errors for the isotopic ratios measured are ±1% for $^{3}He/^{4}He$, ±0.5% for $^{20}Ne/^{22}Ne$, ±1% for $^{21}Ne/^{22}Ne$, ±0.5% for $^{38}Ar/^{36}Ar$, and ±0.2% for $^{40}Ar/^{36}Ar$. Errors in the total concentrations are higher (±10%) for the Murchison carbonaceous chondrite because of the presence of kerogen; however, the concentration ratios are smaller (for example, 3/36) ±2%.
45. The unique formation mechanism required for fullerene to trap high concentrations of noble gases (*17*, *20*, *25*) has further implications for the origin of planetary atmospheres (solar or presolar; produced by degassing of the interior versus late heavy bombardment). After Signer and Suess (*38*) proposed the term "planetary noble gases" for the meteoritic gas component that displays elemental abundances similar to those in the terrestrial atmosphere, it was widely accepted that meteoritic planetary noble gases were the precursors of terrestrial atmospheres. Some workers still favor scenarios where planets acquire most of their volatiles by degassing of the chondritelike building blocks during accretion. Others favor mass-dependent fractionation of a partly solar, partly planetary, noble gas mixture after accretion of the terrestrial planets (*38*). The unique planetary noble gas chemical and isotopic signature measured for the fullerene carrier supports formation in a circumstellar or interstellar environment rather than in the early solar nebula. Although extreme fractionation of a solar gas reservoir may fit the fullerene data, we favor a stellar environment for fullerene synthesis, similar to other known carbon carriers [such as presolar nanodiamonds and silicon carbide (SiC)].
46. Large fullerene cages have limited solubility in solvents such as TMB, and increasing the extraction time and/or temperature only serves to destroy the intact fullerenes. As shown in all of our fullerene studies (*17*, *20*), this TMB- and toluene-extractable component does have noble gas release characteristics similar to those of the unidentified "carbonaceous" meteoritic noble gas carrier. In contrast, nanodiamonds and SiC release their gas at much higher temperatures and/or in the presence of an oxidizer. Fullerene is also the only known extractable pure carbon carrier phase. The noble gas concentrations in Murchison are lower because of dilution with a kerogen component that was not completely separated. Previous measurements of a separated kerogen component showed that it retained no noble gases (*20*).
47. Analysis of the meteorite bulk acid residue after extraction of the fullerenes with TMB and TCB demonstrates that we have extracted only a few percent of the noble gas carrier. Examination of the solvent-extracted bulk acid residue using LDMS indicates that several large fullerene cages (up to C_{800}) are still present in the residue. Thus, we favor the possibility that the bulk of this remaining noble gas carrier in the Murchison and Allende carbonaceous chondrites are in fact large (>C_{100}) fullerenes (*20*).
48. These calculations assume a uniform distribution of the fullerene-encapsulated ^{3}He in a Murchison-type impacting body. An upper limit on the size of the impactor uses the measured fullerene-encapsulated ^{3}He per gram of Murchison versus the measured ^{3}He in the PTB sediments. The lower limit assumes that all of the ^{3}He present in the extracted fraction resides in the fullerene component. For a PTB bolide that is <6 km, there is not enough ^{3}He in Murchison to distribute worldwide in the boundary layer, whereas for a bolide >12 km, the measured ^{3}He for Murchison exceeds the amount measured for the PTB sediments. The Chicxulub impactor is comparable in size, because the concentration of ^{3}He in fullerene at the KTB is similar to that at Sasayama and Meishan.
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